

Effect of core-valence intra-atomic quadrupolar interaction in resonant x-ray scattering at the Dy $M_{4,5}$ edges in DyB_2C_2

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Abstract. The dependence with energy of the resonant soft x-ray Bragg diffraction intensity in DyB_2C_2 for the $(00\frac{1}{2})$ reflection at the Dy $M_{4,5}$ edges have been calculated by using an atomic multiplet hamiltonian including the effect of crystal field and introducing an intra-atomic quadrupolar interaction between the 3d core and 4f valence shell. These calculations are compared with the experimental results (Mulders et al., J. Phys.: Condens. Matter 18 (2006) 11195) in the antiferroquadrupolar and antiferromagnetic phases of DyB_2C_2 . We reproduce all the features appearing $(00\frac{1}{2})$ reflection energy profile in the antiferroquadrupolar ordered phase, and we reproduce the behaviour of the resonant x-ray scattering intensity at different energies in the vicinity of the Dy M_5 edge when the temperature is lowered within the antiferromagnetic phase.

1. Introduction

The charge, orbital, and spin degrees of freedom of the few electrons in the valence states of a material play an important role in its electronic properties. Resonant x-ray scattering (RXS), enhanced by the brightness, tunability, and high degree of polarization available at x-ray synchrotron sources, is an effective technique to measure these microscopic variables. In RXS, by studying intensities at space-group-forbidden reflections, dipolar and quadrupolar order parameters can be studied [1, 2, 3, 4, 5]. Only recently has it become possible to access such ordering phenomena by means of resonant x-ray diffraction. Higher multipolar orderings can be studied by resonant x-ray diffraction: octupoles [7], hexadecapoles [6, 9], anapoles [8, 10]. Also non-resonant x-ray diffraction can give information on higher order multipolar orderings [11].

DyB₂C₂ shows the highest antiferroquadrupole (AFQ) transition with $T_Q = 24.7$ K [12]. The ordering of quadrupoles in DyB₂C₂ has been studied intensively with resonant x-ray scattering [13, 14, 6, 15] and neutron diffraction in magnetic fields [16, 17]. At the AFQ ordering temperature T_Q the space group symmetry of the material is reduced from P4/mbm to P4₂/mmn [18] with a doubling of the unit cell along the c-axis. Below $T_N = 15.3$ K magnetic order appears, which has been observed in neutron diffraction [16, 17]. Inelastic neutron scattering has been used to study the magnetic dipolar and orbital fluctuations in this compound [19]. Mulders et al. [20] report isotropic absorption measurements and soft x-ray resonant diffraction at the $(00\frac{1}{2})$ space group forbidden reflection at the Dy $M_{4,5}$ edges in the antiferroquadrupolar ordered (AFQ) and antiferromagnetic phase (AFM). A possible charge scattering contribution is ruled out, as then s and p incident spectra would differ by orders of magnitude and would have a completely different shape in energy as the Bragg angle is close to 45 degrees. In order to justify the shape of the resonant diffraction energy profile, Mulders et al. [20] use a simple model for describing resonant x-ray scattering in terms of single oscillators for each of the \bar{M} quantum numbers for the $\bar{J} = 5/2, 3/2$ core holes at the $M_{5,4}$ edges. The degeneration of the resonant oscillators would be split due to a Coulomb intra-atomic quadrupolar interaction, given by $[3\bar{M}^2 - \bar{J}(\bar{J} + 1)]Q_{\bar{J}}$, similarly to Mossbauer spectroscopy, and which would be produced by the ordered quadrupolar moment in the 4f shell. A similar core-valence interaction between the valence octupole moment and the core hole was used in NpO₂ [21]. In this paper we explore the effect of such dependence of the core-hole interaction, going beyond the analysis done in [20] by using a full atomic multiplet Hamiltonian including the effect of crystal field.

2. Calculation of the absorption and RXS spectra

We calculate the resonant x-ray scattering factor for the dipolar transition $4f^9 \rightarrow 3d^9 4f^0$ by making use of the program Hilbert++ [22, 23]. The program starts from a model Hamiltonian accounting for multiplets and hybridization, written in terms of creation and destruction operators, and applies Lanczos tridiagonalization to the

Hilbert space spanned by the electronic degrees of freedom of the absorber ion and its nearest neighbours to find the ground state $|g\rangle$. The resonant x-ray scattering tensor is calculated as

$$\langle g | \varepsilon' \mathbf{D} | \frac{1}{\omega - H_e + i\gamma} | \varepsilon \mathbf{D} | g \rangle \quad (1)$$

where H_e is the hamiltonian of the excited state, D is the dipole operator and Γ is the lifetime broadening. We use a model Hamiltonian that includes the atomic multiplets and the crystal field interaction with the neighbouring ions,

$$H = H_{\text{atomic}} + H_{\text{CF}}. \quad (2)$$

Cowan's atomic multiplet program provides ab initio Hartree-Fock values of the radial Coulomb Slater integrals and the spin-orbit interactions for an isolated ion. In order to take into account the screening effects present in the real system with respect to the atomic picture we scale down all the Slater integrals to 75% of their atomic values. To model the interaction with the neighbouring ions, we construct a crystal field term simulating the effect of hybridization with the carbon first neighbour ions,

$$H_{\text{CF}} = \sum_b V_{\sigma,b} f_{z^3}^+ f_{z^3} \quad (3)$$

where V_σ is the energy displacement in the Dy f_{z^3} orbital produced by a ligand ion along the z axis and $f_{z^3}^\dagger/f_{z^3}$ denote creation/destruction operators in the f shell of the Dy ion being the local z axis orientated along the bond direction of each of the neighbouring atoms. This term is summed over the bonding atoms (we consider 8 nearest neighbours). The parameter V_σ is rescaled according to the bond length. We use the available structural information [24, 25] on the environment of first neighbour C ions around a Dy site. Following Adachi et al. [26], in the structure of the quadrupolar ordered phase, we add displacement along the c axis of the positions of the C ions from its positions in the high temperature P4/mbm space group.

In the excited Hamiltonian we introduce a splitting of the core states due to the intra-atomic quadrupole interaction $Q_{\bar{J}}$ [20], $[3\bar{M}^2 - \bar{J}(\bar{J} + 1)]Q_{\bar{J}}$, where $Q_{\bar{J}}$ is the product of the 3d quadrupole moment and the f-electron electric field gradient experienced by the 3d electrons with $Q_{3/2}/Q_{5/2} = \frac{7}{3}$. The introduction of this splitting is necessary due to the difficulty in modeling the crystal field and the interactions that exists in this system, such as the fact that for the 4f shell the point charge model is not good, screening, or the effect of the polarization of the 5d states [27].

The best fit to the x-ray diffraction and absorption spectra taken in the AFQ phase ($T = 18$ K) [20] correspond to the parameters $Q_{5/2} = 0.2$ eV and $V_\sigma = 0.1$ eV. The fitting of the isotropic absorption and the resonant x-ray diffraction energy profile at the reflection $(00\frac{1}{2})$ is shown in Fig. 1. In the plot, we also show the shape that the spectra would have without the core-hole interaction, i.e. $Q_{\bar{J}} = 0$. In the calculated spectra we consider a Boltzmann average in order to take into account the effect of the temperature. It is worth noting that, from the fitting to the experimental spectra we use a positive value of $Q_{5/2} = 0.2$ eV, while in [20], a value of -0.4 eV is used. The change

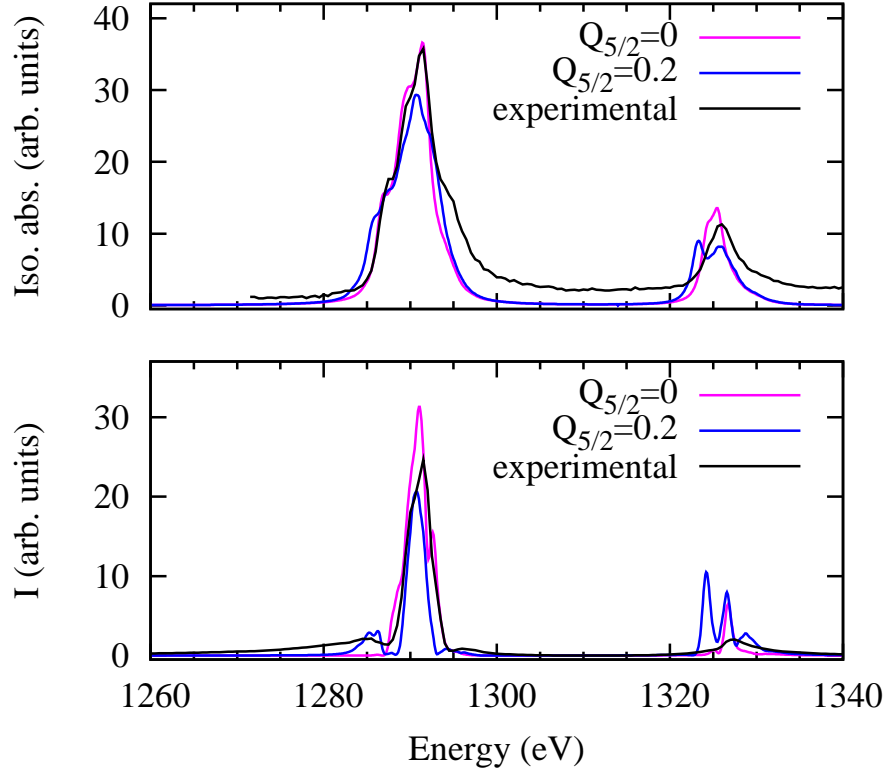


Figure 1. Experimentally measured isotropic absorption and resonant x-ray diffraction spectra at the $(00\frac{1}{2})$ space group forbidden reflection and absorption spectra taken in the AFQ phase ($T=18$ K) [20] together with the calculated spectra, corresponding to the parameter $V_\sigma = 0.1$ eV. Calculated spectra is shown for the cases in which the core-hole interaction is absent ($Q_{5/2} = 0$) and included ($Q_{5/2} = 0.2$ eV).

of sign would mean that the positioning of the harmonic oscillators with different values of \bar{M} in Fig. 2 of reference [20] would be reversed. Using a negative value of $Q_{5/2}$ in our calculation, would lead to a much worse agreement with the diffraction energy profile.

In order to calculate the spectra below $T_N = 15.3$ K in the AFM phase, we calculate the resonant x-ray diffraction spectra introducing an additional term $\mathbf{S} \cdot \mathbf{H}$ term in the Hamiltonian, being \mathbf{S} the spin momentum, and \mathbf{H} a magnetic field wich polarizes the magnetic moment in the ab plane, forming 23 degrees with respect to the a axis. The isotropic absorption does not show any appreciable change when polarizing the magnetic moment. Fig. 2 shows the diffraction energy profile of the Dy M_5 edge for different values of the spin ($S_{\tilde{z}}$) and orbital ($L_{\tilde{z}}$) polarization, where \tilde{z} is the local anisotropy axis in the ab plane. The Boltzmann average does not change significantly the spectra, but it reduces notably the values of $S_{\tilde{z}}$ and $L_{\tilde{z}}$ from the values they would have at $T=0$ K. All the curves in Fig. 2 are normalized to have the same intensity at energies lower than 1282 eV. Our calculated spectra shown in Fig. 2 are consistent with the experimentally determined behavior of the features in the diffraction spectra at $E = 1282$ eV and $E=1291$ eV when lowering the temperature, which is shown in Fig. 1 of reference [20].

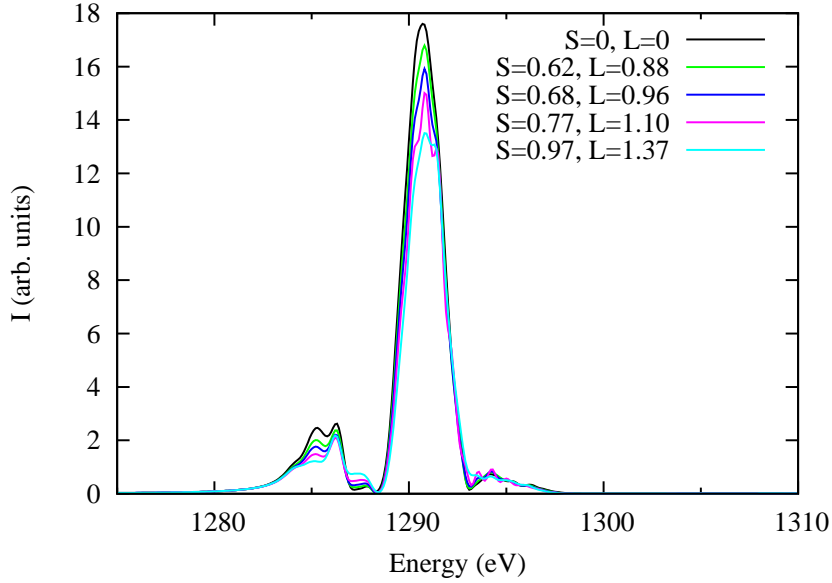


Figure 2. Evolution of the calculated resonant x-ray diffraction spectra in the vicinity of the Dy M_5 edge at the $(00\frac{1}{2})$ space group forbidden reflection when the magnetic moment is polarized in the ab plane forming 23 degrees with respect to the a axis. Spectra are shown for different values of the polarization of the orbital angular momentum L_z and the spin angular momentum S_z . We normalize all the curves to have the same intensity at energies lower than 1282 eV.

3. Conclusions

By using a model taking into account an atomic multiplet Hamiltonian, crystal field and intra-atomic quadrupolar interaction between the 3d core-hole and the 4f valence shell we have reproduced the different features in the experimental isotropic absorption and resonant x-ray Bragg diffraction energy profile at the Dy M_4 and M_5 edges in the antiferroquadrupolar phase of DyB_2C_2 in terms of a dipolar transition ($4f^9 \rightarrow 3d^9 4f^{10}$). When, in our model, we vary the polarization of the magnetic moment of the Dy ion, we observe a variation of the RXS spectra for different energies around the Dy M_5 -edge that agrees with the experimentally observed behaviour of the measured RXS intensities for different energies when the temperature is lowered in the antiferromagnetic phase.

4. Acknowledgements

We thank J.A. Blanco and V. Scagnoli for useful discussions. One of us, J.F.R., is grateful to Gobierno del Principado de Asturias for the financial support from Plan de Ciencia, Tecnologia e Innovacion PCTI de Asturias 2006-2009.

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